



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/GB90/01404 (22) International Filing Date: 11 September 1990 (11.09.90) (30) Priority data: 8921041.3 16 September 1989 (16.09.89) GB (71) Applicant (for all designated States except US): MANCHEM LIMITED [GB/GB]; Ashton New Road, Clayton, Manchester M11 4AT (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : BAKER, Gary [GB/GB]; 56 Glenmore Drive, Failsworth, Manchester M35 9SP (GB). PRINCE, John, William [GB/GB]; 31 Oak Street, Whitworth, Rochdale, Lancashire OL12 8NP (GB).		(74) Agents: LAWRENCE, John, Gordon et al.; McNeight & Lawrence, Regent House, Heaton Lane, Stockport SK4 1BS (GB). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent)*, DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: WATER-BASED WATER REPELLENTS		
(57) Abstract An aqueous water repellent composition comprising the reaction product of one or more of a carboxylic acid or anhydride containing from 3 to 22 carbon atoms and a polyfunctional aromatic or aliphatic amine or substituted amine containing from 2 to 25 carbon atoms and a water soluble metal complex crosslinking agent containing one or more metals selected from Groups Ia, IIa, IIIa, IVa and the first and second rows of transition metals from the Periodic Table of Elements. The composition may contain wax and is dispersed in water to form a water repellent system.		

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WATER-BASED WATER REPELLENTS

This invention relates to aqueous, air drying, water repellent compositions that provide improved long-term water repellency to substrates such as wood and other cellulosic materials, textiles, masonry and concrete. The compositions are also useful in imparting hydrophobicity to powders, for example calcium carbonate, as well as printing inks, adhesives, leather and water-based surface coatings.

Many organic solvent-based coating compositions have been developed which show good water repellency but the use of organic solvents is now a cause for concern on environmental and health grounds. A water repellent system dispersible in water, thus reducing the volatile organic content to a minimum without affecting water repellency properties, is highly desirable.

Aqueous water repellent systems, ie. systems which are dispersible in water, have been developed previously. GB2168394 describes water dispersible compositions useful for preparing aqueous water repellent systems comprising a saturated hydrocarbon wax, at least one oil-soluble metal salt of an organic carboxylic acid, at least one surfactant and at least one hydrocarbon solvent.

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The compositions can be mixed or diluted with water to form the desired aqueous water repellent systems.

According to the present invention there is provided an aqueous water repellent composition comprising the reaction product of one or more of a carboxylic acid or anhydride containing from 3 to 22 carbon atoms and a polyfunctional aromatic or aliphatic amine or substituted amine containing from 2 to 25 carbon atoms, and a water soluble metal complex crosslinking agent containing one or more metals selected from Groups Ia, IIa, IIIa, IVa and the first and second rows of transition metals from the Periodic Table of the Elements.

In particular embodiments of the invention the presence of aqueous acrylic polymers contributes to the stability of the complex compositions as well as giving improved water repellency by additional crosslinking, and possibly a degree of film formation when larger amounts are used.

In a preferred embodiment of the invention, a saturated hydrocarbon wax and/or alkyd resin may be incorporated into the water repellent systems to improve water repellent properties.

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In further embodiments of the invention, small amounts of solubilising agents such as sodium hydroxide or ammonia may be added to improve stability.

The compositions broadly described above are useful in that they can be mixed with water to form water repellent systems stable for long periods when mixed, and find application in imparting water repellency to many materials including, wood, paper, and other cellulosic materials, textiles, masonry, surface coatings, powders, inks, leather and adhesives.

In a typical treatment for imparting water repellency to a wood substrate, it is believed that on contact with the wood a reaction takes place which enables the carboxylic acid and/or amine compound to crosslink with the reactive metal of the metal organic compound to form a water repellent substrate under ambient conditions. Wax, if present as a constituent, adds to the substantivity of the repellency.

A particular advantage of the water repellent systems of the present invention is that the use of undesirable hydrocarbon or other organic solvents is unnecessary to maintain the water repellents in solution. The water repellents of the invention are dispersed in a wholly aqueous medium for use in the treatment of the various substrates.

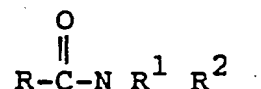
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In preferred aspects of the invention, the carboxylic acid used is a saturated or unsaturated fatty acid exemplified by oleic, isostearic, stearic and ricinoleic acids. Thus an amine soap of isostearic acid was prepared by adding molten isostearic acid at 70°-80°C to an agitated solution of triethanolamine in water. The mixture was agitated for 15 minutes, allowed to cool below 50°C and a zirconium metal crosslinking agent was added to form an example of a water repellent composition according to the invention.

Preferred crosslinking agents may be selected from metal salts of the group comprising zinc, aluminium, titanium, copper, chromium, iron, zirconium and lead and may be exemplified by zirconium complexes as described for example in GB1002103 and, according to one process, prepared by refluxing a carboxylic acid containing 1-4 carbon atoms with a zirconyl carbonate paste and then adding a carboxylic acid containing more than 4 carbon atoms.

Water soluble inorganic metal compounds may also be used. Ammonium zirconium carbonate is particularly preferred for preparing compositions according to the invention.

The broad description above for the manufacture of a typical water repellent complex according to the invention disclosed the use of triethanolamine. Other basic nitrogen-containing organic compounds preferred are also water soluble so as to produce a water dispersible compound when reacted with a carboxylic acid, which may also contain a wax, oil, resin or a mixture thereof. All the nitrogen-containing compounds may be substituted optionally with hydroxyl groups, for example, substituted diols and triols, and may be selected from primary, secondary and tertiary amines containing alkyl groups having 1 to 5 carbon atoms or hydrogen, typified by ethylamine, amino methyl propanol, diethylamine, triethylamine, amino methyl propane diol, amides of the general formula :-



where R, R¹ and R² may be represented by hydrogen or alkyl groups having 1 to 5 carbon atoms and typified by formamide, acetamide, N-ethyl acetamide and N,N dimethyl butyramide, diamines typified by hydrazine and hexamethylene diamine; cyclic amines typified by morpholine and pyridine; aromatic and aliphatic amino acids typified by 3-methyl-4-amino benzoic acid.

As a feature of the invention, a hydrocarbon wax may be incorporated as an emulsion or dispersion. Preferred waxes are paraffin waxes having melting points

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in the range of about 50°C-70°C. These are incorporated by stirring at elevated temperatures in excess of the melting point of the wax.

In previous disclosures waxes have been incorporated into water repellent compositions in organic solvents. In practising the present invention, amounts of paraffin wax representing from 25%-150% weight/weight of the other ingredients present have been successfully incorporated without the need for an organic solvent to aid solution of the wax.

In another aspect, incorporation of an aqueous acrylic polymer such as Glascol LS12, a product available from Allied Colloids, can show improved water repellency as well as improvements in the general stability of the compositions.

Thus, a product according to the invention resulting from the addition of 10% Glascol LS12 to a 1% aqueous solution of the stearate derived from 2-amino-2-methyl-propan-1-ol (AMP) plus 1% Zircomplex PN (a product described in GB1002103) is a low viscosity, milky white liquid with a slight ammoniacal odour. This product shows good water repellent properties when compared with proprietary organic solvent borne water repellents and advantageously has a solids content at least 27% lower than the proprietary products.

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The invention will be further apparent from the following examples.

In each example, a carboxylic acid and an alkanolamine were charged at an equimolar ratio, together or separately with water as required by the formulation, to a suitable reaction vessel. Paraffin wax was then added if required by the product formulation and the mixture heated to 70-75°C with gentle stirring. At 70-75°C the stirring rate was increased to 2,000 rpm and these conditions were maintained for 15 minutes. The reactor contents were then cooled rapidly to below 30°C whilst maintaining a stirring rate of 2,000 rpm. The stirring was then reduced prior to the addition of a metal crosslinker. The crosslinker addition is made in terms of molar ratios of metal to alkanolamine carboxylate, the ratio being determined by the formulation.

The resultant products are stable for storage and suitable for direct application to a substrate.

The following table gives details of the formulations of the different examples :-

Example	Alkanolamine	Carboxylic Acid	Ammonium Zirconium Carbonate	Wax Content as % of Actual Solids	% Total Solids of Application Solution
I	2-amino-2 methyl propan-1-ol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	50.0%	2%
II	2-amino-2 methyl propan-1-ol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	41.2%	1.7%
III	2-amino-2 methyl propan-1-ol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	37.5%	1.6%
IV	2-amino-2 methyl propan-1-ol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	33.3%	1.5%
V	2-amino-2 methyl propan-1-ol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	28.6%	1.4%
VI	2-amino-2 methyl propan-1-ol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	23.1%	1.3%
VII	2-amino-2 methyl propan-1-ol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	0.0%	1.0%
VIII	2-amino-2 ethyl propane 1,3 diol (1.0 moles)	Stearic acid (1.0 moles)	1.0 mole of zirconium	33.3%	1.5%
IX	2-amino-2 ethyl propane 1,3 diol (1.0 moles)	Tall oil fatty acid (1.0 mole)	1.0 mole of zirconium	50%	10%
X	2-amino-2 ethyl propane 1,3 diol (1.0 moles)	Tall oil fatty acid (1.0 mole)	1.0 mole of zirconium	0.0%	5%
XI	3 amino 1,2 propane diol (1.2 moles)	Stearic acid (1.2 moles)	1.0 mole of zirconium	33.3%	1.5%

SUBSTITUTE SHEET

Examples I-VII are particularly suitable for the treatment of wood.

To test water repellency a swelling test was adopted using 18 mm cubes of softwood as follows :-

Each cube treated with water repellent by soaking for 15 minutes in the test solution and air drying for 7-10 days, was placed in a dish beneath a standardised dial gauge. The dial gauge was set to zero and water was added to the dish to totally immerse the test cube.

Dial gauge readings were made at 30 and 120 minute intervals for comparison against a standard. The cube was reweighed to assess the degree of water absorption.

Tests carried out using the products of Examples I-VII gave results as shown in Tables 1 and 2 below :-

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TABLE 1

EXAMPLE	Number of tests conducted	% swell after 30 mins submersion based on original cube size	% swell after 120 mins submersion based on original cube size	% water uptake after 120 mins submersion based on original cube weight
I	5	0.7	1.54	11.4
II	9	0.674	1.6	9.97
III	1	0.575	1.615	9.5
IV	13	0.48	1.58	9.25
V	1	0.536	1.64	9.3
VI	4	0.46	1.31	12.46
VII	8	0.69	1.85	18.2
Comparative*	11	0.56	1.56	10.47
Water	6	0.71	2.32	22.9

* Thompsons Waterseal (Registered Trade Mark)

TABLE 2

EXAMPLE	Number of tests conducted	% reduction in the swell recorded after 30 mins submersion	% reduction in the swell recorded after 120 mins submersion	% reduction in the water uptake of the treated cube after 120 mins submersion
I	5	-1.4	-33.6	-50.2
II	9	-5.1	-31.0	-56.5
III	1	-19.0	-30.4	-58.5
IV	13	-32.4	-31.9	-59.6
V	1	-24.5	-29.3	-59.4
VI	4	-35.2	-43.5	-45.6
VII	8	-2.8	-20.3	-20.5
Comparative*	11	-21.1	-32.8	-54.3
Water	6	0	0	0

* Thompsons Waterseal (Registered Trade Mark)

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The formulation of Example VIII is particularly suitable for the treatment of textiles.

To test water repellency, samples of cotton fabric (1x0.5m) were immersed in either the formulation (test) or water (control) for 5 minutes and oven dried at 80°C for 10 minutes. Spray rating tests were carried out to British Standard 3702. A spray rating of less than 4 fails. Maximum possible rating is 5.

	Spray Rating
Test	5
Control	2

Example VIII is also suitable for the treatment of adhesives.

To test water repellency, an adhesive (polyvinyl acetate), was mixed with either the formulation (test) or water (control) in a 1:1 ratio and Whatman No 1 filter paper discs soaked and oven dried for 15 minutes at 95°C. Hydrostatic head tests (HHT) were then carried out.

	HHT (cm)
Test	34
Control	16

The formulation of Example IX is particularly suitable for the treatment of brick, concrete, ink, leather and chipboard.

To test water repellency of brick and concrete, suitably sized test pieces were soaked in the formulation (test) or water (control) and allowed to dry for 7 days and accurately weighed. The pieces were then immersed in water for 1 hour, dabbed dry and re-weighed.

		% wt increase	% reduction in absorbance
Brick	Test	1.6	83.5
	Control	9.7	
Pre-cured Concrete	Test	0.5	93.2
	Control	7.3	

To test water repellency of ink, solutions were made up mixing Quink black ink with either the formulation (test) or water (control) in a 1:1 ratio. Whatman No 1 filter paper discs were soaked in the solutions and air dried for 48 hours. Hydrostatic head tests were then carried out.

	HHT (cm)
Test	24.5
Control	1.0

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To test water repellency of leather, small pieces (2x3cm) were soaked in either the formulation (test) or water (control) for 5 minutes and allowed to dry for 5 days before accurately weighing. the pieces were then submerged in water for 1 hour, dabbed dry and re-weighed.

% water absorbed		% reduction of control
Test	90.4	23.8
Control	118.6	

To test water repellency of chipboard, samples (5x5x1.1cm) were soaked in either the formulation (test) or water (control) for 15 minutes and dried for 72 hours before accurately weighing. Samples were then submerged in water for 24 hours and the percentage swell and water absorption were determined.

% swell after submersion		% water absorption based on original wood weight
Test	15.0	47.4
Control	27.1	

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The formulation of Example X is particularly suitable for the treatment of powders.

To test water repellency, 10g of calcium carbonate, either pre-treated with the formulation (test) or untreated (control), was added to 200ml of water and agitated vigorously for 30 seconds causing the calcium carbonate to 'wet out' and sink to the bottom. The water containing the 'wet' calcium carbonate was then filtered through pre-weighed filter paper, dried at 35C for 48 hours and re-weighed.

	wt wetted	% not wetted
Test	0.1	99
Control	9.7	3

The formulation of Example XI is particularly suitable for the treatment of paper to give both water repellency and enhanced tensile strength.

To test water repellency, Whatman No 1 filter paper discs were soaked in either the formulation (test) or water (control), oven dried at 110°C for 30 minutes before hydrostatic head tests were carried out.

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	HHT (cm)
Test	100
Control	15

To test wet tensile strength a 555g weight was used to apply stress to the filter paper discs (5.5cm Dia) and the time taken for the paper discs to fracture recorded.

	Average time to shear (min/sec)
Test	4-59
Control	0

It will be appreciated that it is not intended to limit the invention to the above examples only, many variations, such as might readily occur to one skilled in the art, being possible, without departing from the scope thereof as defined by the appended claims.

CLAIMS

1. An aqueous water repellent composition comprising the reaction product of one or more of a carboxylic acid or anhydride containing from 3 to 22 carbon atoms and a polyfunctional aromatic or aliphatic amine or substituted amine containing from 2 to 25 carbon atoms and a water soluble metal complex crosslinking agent containing one or more metals selected from Groups Ia, IIa, IIIa, IVa and the first and second rows of transition metals from the Periodic Table of Elements.
2. A composition according to claim 1, including a saturated hydrocarbon wax.
3. A composition according to claim 1 or claim 2, including an alkyd resin.
4. A composition according to any preceding claim, including an aqueous acrylic polymer.
5. A composition according to any preceding claim, including a solubilising agent.
6. A composition according to any preceding claim, wherein the crosslinking agent comprises Ammonium Zirconium Carbonate.

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7. A composition according to claim 6, wherein the carboxylic acid is stearic acid.

8. A composition according to claim 7, wherein the amine is 2-amino-2-methyl-propan-1-ol.

9. A composition according to claim 7, wherein the amine is 2-amino-2-ethyl-propane 1, 3 diol.

10. A composition according to claim 6, wherein the amine is 3-amino 1,2 propane diol.

11. A composition according to claim 6, wherein the carboxylic acid is Tall Oil fatty acid.

12. A composition according to claim 11, wherein the amine is 2-amino-2-ethyl-propane 1, 3 diol.

13. A composition according to any one of claims 6-12 wherein paraffin wax is present in an amount from 0.0% - 50% by weight of solids.

14. A water repellent system comprising the composition according to any preceding claim dispersed in water.

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15. A water repellent system according to claim 14, wherein the weight of solids in the solution is in the range of from 1% - 10% .

16. A method of treating a substrate to render it water repellent comprising the steps of applying thereto a composition as claimed in any one of claims 1 to 15.

17. A method according to claim 16, in which the substrate is wood.

18. A method according to claim 16, in which the substrate is a textile.

19. A method according to claim 16, in which the substrate is an adhesive.

20. A method according to claim 16, in which the substrate is masonry.

21. A method according to claim 16, in which the substrate is cement.

22. A method according to claim 16, in which the substrate is ink.

23. A method according to claim 16, in which the substrate is leather.

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24. A method according to claim 16, in which the substrate is chipboard.

25. A method according to claim 16, in which the substrate is a powder.

26. A method according to claim 16, in which the substrate is paper.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01404

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 09 K 13/18																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁵</td> <td style="padding: 5px;">C 09 K</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	C 09 K											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category ⁹</th> <th style="width: 70%; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;"> EP, A, 0257720 (UNION CARBIDE CANADA LTD) 2 March 1988 see page 4, lines 1-20; example 6; claims <div style="text-align: center;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-5,8-14</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;"> EP, A, 0070983 (RÖHM GmbH) 9 February 1983 see page 1, line 1 - page 2, line 10; page 7, line 20 - page 8, line 26; claims <div style="text-align: center;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-5,8-14</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;"> US, A, 3912674 (R.E. STAHL) 14 October 1975 see column 1, line 45 - column 3, line 2; claims <div style="text-align: center;">---</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,4,5,13,18</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 10px;">./.</td> </tr> </tbody> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	EP, A, 0257720 (UNION CARBIDE CANADA LTD) 2 March 1988 see page 4, lines 1-20; example 6; claims <div style="text-align: center;">---</div>	1-5,8-14	Y	EP, A, 0070983 (RÖHM GmbH) 9 February 1983 see page 1, line 1 - page 2, line 10; page 7, line 20 - page 8, line 26; claims <div style="text-align: center;">---</div>	1-5,8-14	Y	US, A, 3912674 (R.E. STAHL) 14 October 1975 see column 1, line 45 - column 3, line 2; claims <div style="text-align: center;">---</div>	1,4,5,13,18	./.		
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center; padding: 5px;">11th December 1990</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; padding: 5px;">22. 01. 91</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px;"> International Searching Authority <div style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; padding: 5px;"> Nuria TOPIC </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; padding: 5px;">11th December 1990</div>	Date of Mailing of this International Search Report <div style="text-align: center; padding: 5px;">22. 01. 91</div>	International Searching Authority <div style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; padding: 5px;"> Nuria TOPIC </div>											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	DE, A, 3215936 (CHEMISCHE FABRIK PFERSEE GmbH) 3 November 1983 see page 3, line 10 - page 4, line 13; claims ---	1,4,5,13,18
A	US, A, 4360385 (GRUNEWALDER) 23 November 1982 see abstract; claims ---	1-5,17
A	EP, A, 0216297 (MITSUBISHI CHEMICAL IND.) 1 April 1987 see abstract, claims ---	1-5
A	GB, A, 1002103 (HARDMAN & HOLDEN LIMITED) 25 August 1965 see page 1, lines 25-46; claims 1,9-15 cited in the application ---	1
A	GB, A, 2168394 (MOONEY CHEMICALS INC.) 18 June 1986 see abstract; claims cited in the application -----	1-5

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9001404
SA 40124

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EP-A- 0216297	01-04-87	JP-A- 62070479 JP-A- 62081452 JP-A- 62083345 US-A- 4748196 AU-B- 588916 JP-A- 62181384	31-03-87 14-04-87 16-04-87 31-05-88 28-09-89 08-08-87
GB-A- 1002103		None	
GB-A- 2168394	18-06-86	US-A- 4612255 AU-A- 5082185 CA-A- 1249901 SE-A- 8505961	16-09-86 26-06-86 14-02-89 19-06-86

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C09K 3/18	A1	(11) International Publication Number: WO 91/04305 (43) International Publication Date: 4 April 1991 (04.04.91)
(21) International Application Number: PCT/GB90/01404 (22) International Filing Date: 11 September 1990 (11.09.90) (30) Priority data: 8921041.3 16 September 1989 (16.09.89) GB (71) Applicant (for all designated States except US): MANCHEM LIMITED [GB/GB]; Ashton New Road, Clayton, Manchester M11 4AT (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : BAKER, Gary [GB/GB]; 56 Glenmore Drive, Failsworth, Manchester M35 9SP (GB). PRINCE, John, William [GB/GB]; 31 Oak Street, Whitworth, Rochdale, Lancashire OL12 8NP (GB).		(74) Agents: LAWRENCE, John, Gordon et al.; McNeight & Lawrence, Regent House, Heaton Lane, Stockport SK4 1BS (GB). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent)*, DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With a revised version of the international search report.</i> (88) Date of publication of the revised version of the international search report: 3 September 1992 (03.09.92)
(54) Title: WATER-BASED WATER REPELLENTS (57) Abstract An aqueous water repellent composition comprising the reaction product of one or more of a carboxylic acid or anhydride containing from 3 to 22 carbon atoms and a polyfunctional aromatic or aliphatic amine or substituted amine containing from 2 to 25 carbon atoms and a water soluble metal complex crosslinking agent containing one or more metals selected from Groups Ia, IIa, IIIa, IVa and the first and second rows of transition metals from the Periodic Table of Elements. The composition may contain wax and is dispersed in water to form a water repellent system.		

* (Referred to in PCT Gazette No. 23/1992, Section II)

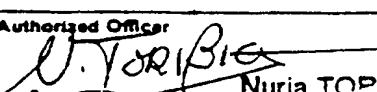
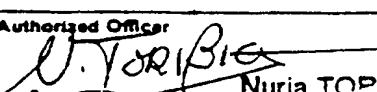
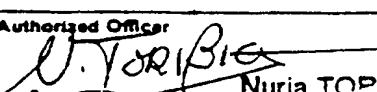
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ES	Spain				

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01404

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 09 K 3/18														
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ Classification System I Classification Symbols IPC ⁵ C 09 K Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸														
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1"> <thead> <tr> <th>Category ¹⁰</th> <th>Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th>Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>EP, A, 0257720 (UNION CARBIDE CANADA LTD) 2 March 1988 see page 4, lines 1-20; example 6; claims ---</td> <td>1-5,8-14</td> </tr> <tr> <td>Y</td> <td>EP, A, 0070983 (ROHM GmbH) 9 February 1983 see page 1, line 1 - page 2, line 10; page 7, line 20 - page 8, line 26; claims ---</td> <td>1-5,8-14</td> </tr> <tr> <td>Y</td> <td>US, A, 3912674 (R.E. STAHL) 14 October 1975 see column 1, line 45 - column 3, line 2; claims ---</td> <td>1,4,5,13,18</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	EP, A, 0257720 (UNION CARBIDE CANADA LTD) 2 March 1988 see page 4, lines 1-20; example 6; claims ---	1-5,8-14	Y	EP, A, 0070983 (ROHM GmbH) 9 February 1983 see page 1, line 1 - page 2, line 10; page 7, line 20 - page 8, line 26; claims ---	1-5,8-14	Y	US, A, 3912674 (R.E. STAHL) 14 October 1975 see column 1, line 45 - column 3, line 2; claims ---	1,4,5,13,18
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<p>¹⁴ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>														
IV. CERTIFICATION <table border="1"> <tr> <td>Date of the Actual Completion of the International Search 11th December 1990</td> <td>Date of Mailing of this International Search Report 22.01.91</td> </tr> <tr> <td>International Searching Authority EUROPEAN PATENT OFFICE</td> <td>Signature of Authorized Officer  Nuria TORIBIO</td> </tr> </table>			Date of the Actual Completion of the International Search 11th December 1990	Date of Mailing of this International Search Report 22.01.91	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer  Nuria TORIBIO								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	DE, A, 3215936 (CHEMISCHE FABRIK PFERSEE GmbH) 3 November 1983 see page 3, line 10 - page 4, line 13; claims ---	1,4,5,13,18
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